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HIGH-VELOCITY CRACKING OF LIQUID HYDROCARBONS

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High-velocity cracking represents the decomposition of hydrocarbons under such conditions that there is a rapid rate of external heat exchange combined with a short time of reaction at high temperatures. Let us examine some of the characteristics of cracking at high temperatures. In the first place, as the temperature is raised, the rates of all reactions taking place during thermal cracking are sharply increased. We will clarify what changes this will bring about aside from generally intensifying the process. The first stage of the reaction in the high-temperature cracking of most types of mineral oils consists of destruction with the formation of saturated and unsaturated compounds having a shorter hydrocarbon chain, and condensation reactions of compounds obtained as a result of the destruction. In other words, the process of the formation of undesirable products with an extensive degree of condensation (i.e., of coke) from crude oil during cracking can be interpreted fundamentally as a consecutive reaction in which the desirable compounds act as intermediate products [1].

It is known that the maximum yield of the intermediate products depends on the ratios of the individual reaction velocities, i.e., in this case on the ratio of the velocity of the destruction reaction to that of the coke-forming reaction. On the basis of experiments on the cracking of light gaseous hydrocarbons [2] and of heavy oils with short contact durations, under the conditions of rapid heat exchange, and also on the basis of published data [3, 4], we established that the formation of products of extensive condensation (coke) takes place at a slower rate than the destruction reaction. Since the rate of the first process (coke formation) increases with increasing temperature relatively slowly, the difference between the two rates will grow larger at elevated temperatures (see also [8]). From the kinetic point of view, this is due to the fact that the reaction for the formation of carboids, as does every process that forms a new solid phase, requires multiple collisions and has a comparatively low activation energy.

Analysis of our experiments and those described in the literature [3, 4] indicates, in agreement with what has been stated, that as the temperature is increased, the amount of products of extensive condensation formed during cracking with a degree of conversion that is not too high, not only does not increase, but even decreases. Thus, by selecting a sufficiently short reaction time and by using recirculation, it is possible to raise the temperature and greatly increase the rate of thermal cracking without increasing the yield of coke. Of the other characteristics of the chemistry of cracking at high temperatures, one should also note the well-known fact that as the temperature is raised, the fraction of unsaturated and aromatic compounds in the cracking products increases as a result of displacement of the equilibria involved.

The study of cracking at high temperatures is closely tied in with the problem of achieving a rapid transfer of considerable quantities of heat into the zone of the reaction for rapid heating of the products being cracked. It is necessary to resort to the well-known method of transferring heat by direct contact with particles of a heat carrier, i.e., by external heat exchange. Rapid heating by using particles of a heat carrier also has its limits of applicability however. It obviously cannot be used with temperatures and process duration times at which the time of heating becomes commensurate with the time of the reaction. Until now no one has examined this problem specifically and inasmuch as the disregard of this circumstance lowers the value of a number of

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other works, we will examine this question in the light of its bearing on the applicability of high-velocity cracking. With this aim in view, we will estimate the minimum time required for heating in rapid cracking by using the theory of similarity.

Let us assume that the amount of the previously heated stationary heat carrier (particles having an effective diameter d) is many times greater by weight than the amount of the product to be heated. Let us assume that the product, after first being heated in the conventional way to the temperature T_0 , at which the reaction proceeds sufficiently slowly, is required to be heated rapidly to 200-300 degrees. We will assume that the heat-transfer coefficients for the product to be cracked will be equal to some value

$$D = \frac{\lambda}{c\rho} = \gamma = a$$

corresponding to an average temperature where λ is the coefficient of heat conductivity, γ the coefficient of kinematic viscosity, ρ the density, and c the specific heat capacity at constant pressure.

On the basis of Z. F. Chukhanov's formula [9], and neglecting heat transfer by radiation, we find that the coefficient of heat transfer is equal to:

$$\alpha = \frac{Nu_{\alpha} \rho}{d} \approx 0.24 \frac{a}{d} \rho (Re)^{0.83} (Re > 100), \quad (1)$$

or

$$\alpha = 0.24 \left(\frac{a}{d}\right)^{0.17} V^{0.83} c \rho, \quad (2)$$

where V is the linear velocity of flow around the particles. Since we stipulated that the amount of heat carrier will be many times greater than that of the product to be heated, we can neglect changes in the temperature of the heat carrier T_t while estimating the heating time. In this case

$$c \frac{d(T - T_t)}{dt} = \alpha S (T - T_t) \quad (3)$$

where S is the surface of the heat carrier as compared to the unit mass of the product being heated. Integrating (3) and taking as the time of heating the time Θ in which the difference $T - T_t$ decreases by the factor of e , we find that

$$\Theta = \frac{c}{\alpha S} = \frac{1}{0.24 \frac{a}{d} \rho V^{0.83}} \left(\frac{d}{a}\right)^{0.17} \quad (4)$$

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With the aid of simple considerations we find that

$$s = \frac{6}{d\rho} \frac{1-\gamma}{\gamma} \quad (5)$$

(where γ is the degree of dispersion). From this we obtain a formula for the heating time:

$$\theta = \frac{d^{1.17}}{1.44 \cdot v^{0.83}} \frac{\gamma}{1-\gamma} \quad (6)$$

Formula (6) holds when Re is greater than 100 and under such conditions that the ratio of the weight of the heat carrier to the weight of the heated product is greater than one. The expression for the heating time (6) depends very little on the magnitude of the coefficient of transfer α , which is characteristic for processes having a well-developed turbulence. In the case under consideration, a 0.17 is always equal to 1 (cm⁷ sec), hence the heating time is determined only by the diameter of the particles and the rate of flow and is practically independent of the properties of the product being heated. When Re is less than 100, formula (6) ceases to be correct. Instead, when Re is less than 10 and Nu is constant and equal to 2, another expression is obtained

$$\theta = \frac{d^2}{12\alpha} \frac{1-\gamma}{\gamma} \quad (7)$$

When Re is greater than 10 but less than 100, one can interpolate between formulas (6) and (7). The expressions for the heating time, (6) and (7), indicate that under the conditions of rapid cracking, θ has a value of the order of 10^{-4} seconds.

Of special interest is the rapid cracking of heavy oils, where it is expedient to dilute them with gaseous hydrocarbons or steam. This allows the yield of coke to be decreased and at the same time increases the yield of the liquid fractions. We note that the use of gaseous solvents in the chemical destruction of heavy oils has been widely adopted [1, 6, 7].

It appears that rapid cracking of heavy petroleum products is best accomplished at temperatures of the order of 700 degrees and with a contact time of 0.1 second. It is therefore necessary to heat the crude material very rapidly and cool the products of cracking very rapidly in order to maintain the intended reaction time. In Table 2 are listed the results of experiments carried out in a special installation with a moving heat carrier on three types of heavy crude materials whose characteristics are given in Table 1 (with recirculation of the residue). The characteristics of the distillates obtained are listed in Table 3. As seen in Table 3 the distillation fractions obtained contain a large amount of unsaturated and sulfur compounds; as a result of reforming these distillates under the conditions of the aromatization process, a high-quality, stable product is obtained. The 205-360 degree fraction of high-velocity cracking is best subjected to hydrogenation over a stationary catalyst.

Table 1. Physicochemical Properties of the Initial Crude Material

										<u>Fractional Comp in % by Wt</u>				
<u>Crude</u> <u>Material</u>	<u>d</u> ₂₀ <u>4</u>	<u>Elemental Comp</u> <u>in % by Wt</u>				<u>% Asphalt-</u> <u>enes</u>	<u>Excise</u> <u>Tars</u>	<u>Initial</u> <u>Boiling</u> <u>Temp (deg)</u>						
		<u>C</u>	<u>H</u>	<u>S</u>	<u>N</u>				<u>350-</u> <u>400°</u>	<u>400-</u> <u>425°</u>	<u>425°</u>	<u>Losses</u>		
No 1	1.0839	85.2	9.2	3.4	0.54	29.0	--	--	350°	350- 400°	400- 425°	425°	Losses	
No 2	0.9510	85.5	11.4	2.4	0.50	7.0	65.0	150	10.5	8.5	75.0	76.0	--	
No 3	0.8967	--	--	1.77	--	0.41	20.0	310	11.6	44.7	39.7	3.0	1.0	

Table 2. High-Velocity Cracking With a Heat Carrier

Crude Material	Temp in Degrees of the end of Boiling of Fractions Being Taken off	Temp of Added Heat Carrier (deg)	Temp at Center of Reactor (deg)	Reaction time (sec)	Coef of Recirculation	Amount of Circulating Gas in % of Load	Yield in Wt % of Crude Material			
							Fractions Boiling Off		Gas and	Losses
							Below 205°	205-360°		
No 1	205	915	670	0.13	2.0	13.8	28	-	31	41
No 2	360	900	700	0.10	2.0	13.8	29	48	6.2	16.8
No 3	205	930	690	0.12	3.0	18.0	61	-	5	34

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Table 3. Properties of Distillates of High-Velocity Cracking

Fractions	Crude Material No 1			Crude Material No 2				Crude Material No 3				
	d ₂₀ 4	% Sulfo- nizable	Iodine No by Margoshes' Method	% S	d ₂₀ 4	% Sulfo- nizable	Iodine No by Margoshes' Method	% S	d ₂₀ 4	% Sulfo- nizable	Iodine No by Margoshes' Method	% S
With end of boiling at 205°	0.7869	91.9	198.3	0.8	0.8012	36.0	173	0.5	0.7984	95.0	143.0	0.5
Boiling at 205- 360°	0.9311	89.0	58.1	--	0.9160	68.0	41	1.2	0.9244	76.0	44.7	1.7
Boiling above 360°	1.0613	--	--	3.8	1.050	--	--	2.4	1.021	--	--	--

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